REMARKS

I.   Preliminary Matters

Claims 3-33 are pending in the application. Applicants thank the Examiner for indicating

that claims 12-19 are allowed, and claims 21-23, 26-27, 30 and 32 would be allowable if

rewritten in independent form including all of the limitations of the base claim and any

intervening claims.

Claim 3 is amended to recite that the metal particle is one per independent pattern.

Claim 10 is amended accordingly, to delete the above limitation from the claim.

No new matter is added, and Applicants believe that the amendment to claim 3 places

the application in condition for allowance. Accordingly, Applicants respectfully request

entry of the Amendment after final as appropriate.

II.   Response to Claim Rejection Under 35 U.S.C. § 102

Claims 3-11, 20 and 24-25 are rejected under 35 U.S.C. § 102 (b) as allegedly being

anticipated by Japanese Patent 2002-285335 A (hereafter "JP '335".)

Applicants respectfully traverse.

Amended claim 3 recites, in part, a method for fixing a metal particle, such that the metal

particle is one per independent pattern. The presence of one metal particle per independent

pattern is also discussed in the specification, for example, at page 11, lines 8-10. Additionally,

Applicants submit herewith "Diameter-Controlled Carbon Nanotubes Grown from

Lithographically Defined Nanoparticles"[1], Ishida et al., Japanese Journal of Applied Physics,

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[1] No IDS is required to submit and have the reference be considered by the Examiner because the reference is submitted as evidence directed to an issue of patentability raised in an Office Action and is timely presented. MPEP 609.05(c).

Vol. 43, No. 10B, 2004, pp. L1356-L1358, to demonstrate the presence of one metal particle per independent pattern.

JP '335 does not teach a method for fixing a metal particle where the metal particle is one per independent pattern. Therefore, JP '335 does not teach each and every element of present claim 3, and claim 3 is patentable over JP '335. Claims 4-11, 20-27, 30 and 32 are also patentable, at least by virtue of their dependence from claim 3. Accordingly, Applicants respectfully request reconsideration and withdrawal of the § 102 rejection of claims 3-11, 20 and 24-25 and the objection to claims 21-23, 26-27, 30 and 32.

Conclusion

In view of the above, reconsideration and allowance of this application are now believed to be in order, and such actions are hereby solicited. If any points remain in issue which the Examiner feels may be best resolved through a personal or telephone interview, the Examiner is kindly requested to contact the undersigned at the telephone number listed below.

The USPTO is directed and authorized to charge all required fees, except for the Issue Fee and the Publication Fee, to Deposit Account No. 19-4880. Please also credit any overpayments to said Deposit Account.

Respectfully submitted,

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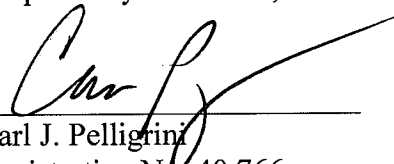
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11

Diameter-Controlled Carbon Nanotubes Grown from Lithographically Defined Nanoparticles

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We report the novel synthesis method of iron nanoparticles that can easily control both position and diameter significantly smaller than the lithography limit, and also demonstrate diameter- and position-controlled carbon nanotube (CNT) growth from the nanoparticles. We patterned iron particles having a 1.7 ± 0.6 nm diameter distribution within a positioning accuracy of ± 5 nm by means of the "lithographically-anchored nanoparticle synthesis (LANS)" method. CNTs were grown by chemical vapor deposition using ethanol. A catalyst activity of $\sim 10\%$ and a CNT diameter distribution of 1.3 ± 0.4 nm were obtained. Raman spectroscopy revealed the presence of single-walled CNTs. [DOI: 10.1143/JJAP.43.L1356]

KEYWORDS: carbon nanotube, nanoparticle, chemical vapor deposition, Raman spectroscopy, electron beam lithography, electron beam resist

Single walled carbon nanotubes (SWNT) have attracted a great deal of attention because of their unique one-dimensional conductive properties and physical and chemical peculiarity.[1-6] Various studies have demonstrated that the geometric features of these carbon nanotubes (CNTs) can be controlled statistically such as positioning, orientation, diameter, length, and chirality,[7-12] making them easy to incorporate into devices at a high yield. Controlling the diameter with catalysts within a range of 1 nm has particularly been recognized as indispensable in growing SWNTs selectively by using chemical vapor deposition (CVD).[9,10] However, many technological issues still remain in controlling and characterizing "individual" CNTs because most studies on CNT growth have been and are still using randomly dispersed catalysts over the growth area.[7-12] In such case, nanoparticles coalesce with each other to give various particle sizes. Also, there is a difficulty in positioning each of them separately.

Here, we describe the results of diameter- and position-controlled iron nanoparticle synthesis by using a novel lithographically-directed technique and also demonstrate CVD growth of CNTs from the nanoparticles. This method could easily control the particle diameter considerably smaller than the lithography limit and also their positions by using a small resist pattern as a nano-sized vessel for the bottom-up nanoparticle synthesis namely the "lithographically-anchored nanoparticle synthesis (LANS)" method.

The synthesis process is schematically illustrated in Figs. 1(a)–1(d). We used p-methyl methylacetoxy calix[6]-arene (MC6, Tokuyama Corp.) for the base resist material.[13] MC6 is a high-resolution negative electron beam (EB) resist consisting of C, O, and H atoms.[13] We used Fe(III) acetylacetonate (FeAcac3, Aldrich) for the metal source. MC6 (typically 1.0 wt%) and FeAcac3 (typically 0.1 wt%) were dissolved in monochlorobenzene and stirred for 1 hr. The well mixed resist solution was filtered through a 0.2-μm Teflon membrane filter (Millipore, SLFG025-50). The Fe-doped resist films were prepared by spin-coating the resist solution on a silicon dioxide substrate at 3000 rpm, and prebaking the film in dry N_2 ambient at 100°C for 1 hr (Fig. 1(a)).

The EB lithography system used in this work was a direct EB writing system JBX-5EF (JEOL Ltd.) operating at $V_{acc} = 50$ keV and $I = 100$ pA. After exposure, the resist patterns were developed in xylene for 30 s and rinsed in IPA
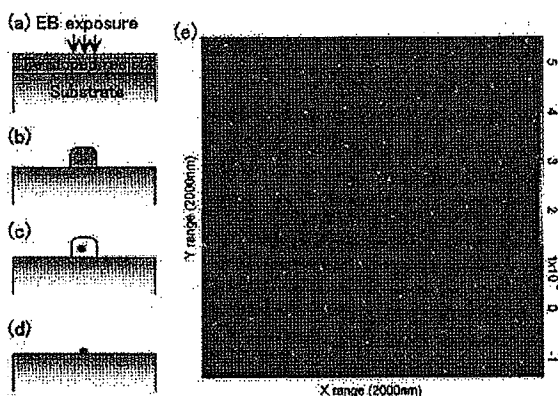

Fig. 1. Synthesis process for nanoparticles. (a) Disperse organometallic compound uniformly in negative resist solution and prepare film. (b) Expose to electron-beam (EB) to produce pattern for metal-containing non-equilibrium amorphous carbon. (c) Anneal pattern to transform it into equilibrium state and cause segregation of metal or metal compound particles in pattern. (d) Remove residual carbon resin by exposing it to oxygen plasma or high temperature oxygen. (e) AFM image of Fe nanoparticle array patterned at 200-nm pitch. Average dot height was estimated at 4.0 nm (standard deviation of 0.9 nm). Image size is 2×2 μm. Z scale bar is indicated at right edge of image.

for 10 s, and the wafer was dried using an N_2 blow gun. We could obtain a resist dot with a typical diameter of 20 nm and a height of 20 nm when 10^6 electrons were exposed per dot (Fig. 1(b)).

Exposing the resist film and organometallic molecules to EB turned them into non-equilibrium amorphous carbon resin, which contained excessive Fe atoms to the solid solubility. To form Fe nanoparticles in a resist pattern, the substrate was then loaded in a quartz tube evacuated below 10^{-4} Pa and annealed at 650–800°C for 5–30 min in an electric furnace. Thermal annealing was done to transform the amorphous carbon into an equilibrium state and to segregate the metal or metal compound particles in the pattern (Fig. 1(c)). The amorphous carbon surrounding Fe particles was thought to be transformed into polycrystalline graphite due to the catalytic effect of Fe.[14,15]

After annealing, Fe particles were still covered with graphite carbon. To remove residual carbon, the substrate was exposed to oxygen plasma or high-temperature oxygen (400°C). Finally, only metal particle remained on the point

where the original resist pattern had been formed (Fig. 1(d)).

The advantage of the LANS method is that the metal particle size can be effectively controlled considerably below the lithography limit due to the original content of the organometallic compound and the size of the resist pattern. Also, the position of particles can be precisely controlled at the same time. In addition, it can be applied to all metals forming an exclusive mixture with carbon at the equilibrium state.

Figure 1 (e) is an AFM image of an Fe particle array patterned at 200-nm pitches on a SiO_2 substrate. The FeAcac3 content in the resist solution was 0.1 wt%. Thermal annealing was done at 650°C for 5 min. The residual carbon was removed by exposing it to 400°C air for 30 min. The average of Fe particles height and standard deviation were estimated to be 4.0 nm and 0.9 nm, respectively. Particles were evident at each lattice point. Most had a spherical outline, but some were deformed or split in two.

To confirm what the particles consisted of, we inspected them with high-resolution transmission electron microscopy (HR-TEM). Some images revealed an ordered structure (Fig. 2). Their size was about 3 nm. The lattice spacing of 0.20 nm was close to that of α-Fe (110). However, most TEM images did not reveal a clear lattice but a disordered silhouette with a few layers of ordered structures. Electron diffraction analysis confirmed the diffraction rings corresponded to Fe_2O_3 and Fe_3C. These results indicated that the particles form a mixture of α-Fe, Fe_2O_3, and Fe_3C.

To fabricate iron catalyst particles for the CNT-CVD growth, we prepared a mixed resist solution of MC6 (0.75 wt%) and FeAcac3 (0.2 wt%). Thermal annealing was done at 800°C for 30 min. Residual carbon was removed by exposing it to oxygen plasma for 5 min. As a result, arrayed Fe particles with an average height of 1.7 nm and a standard deviation of 0.6 nm were obtained. The size uniformity obtained by the LANS method was comparable with conventional liquid-phase synthesis methods.[7,8,16] In

addition, outstanding positioning accuracy within ± 5 nm (roughly estimated from AFM image) was achieved.

Carbon nanotubes (CNTs) were grown from 1.7-nm particles with ethanol CVD. The substrate was first heated up to 750°C in an evacuated quartz tube (approx. 10^{-4} Pa) in an electric furnace. After closing the valve between the vacuum pump and quartz tube, ethanol vapor (approx. 10^3 Pa) was introduced into the tube. After growth for 1 min, the ethanol was evacuated and the substrate was cooled, both immediately.

Figure 3 is an AFM image of CNTs grown from an Fe catalyst array (100-nm pitch). Most CNTs apparently grew from the patterned particles. This indicated that this system favored a root-growth mechanism. The direction the CNTs grew seemed random. Their length also randomly ranged from several tens of nanometers to over 2 μm, which increased as the growth time was extended. The activity of the catalyst particles were easily quantified in this method and found to be about 10% under these growth conditions. After growth, the particles moved slightly due to thermal excitation and most expanded from their original size probably due to amorphous carbon deposition or graphite carbon precipitation.[14,15]

We also investigated the relationship between the catalyst particle size and the diameter of CNTs. Figure 4 plots diameter distributions for catalyst particles and CNTs. The average diameter and standard deviation 1σ were 1.7 nm and 0.6 nm for catalysts, and 1.3 nm and 0.4 nm for CNTs, respectively. The diameter distribution of CNTs was wholly included in that of catalysts, but shifted to a smaller diameter. The peak shift might indicate that the CNTs grew specifically with a smaller diameter than the catalysts, or that the CNTs were grown only from small particles under the CVD conditions.

Raman spectra collected from three different points with 632.8-nm excitation are shown in Fig. 5. Radial breathing mode (RBM) peaks were obtained from these three points from 100 different scans over the patterned area using a
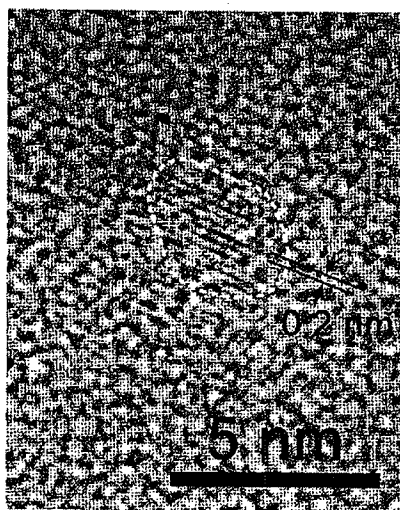

Fig. 2. HR-TEM image of Fe nanoparticle, which was taken through thin SiO_2 membrane. Particle of about 3 nm indicated ordered structure with lattice spacing of 0.20 nm.
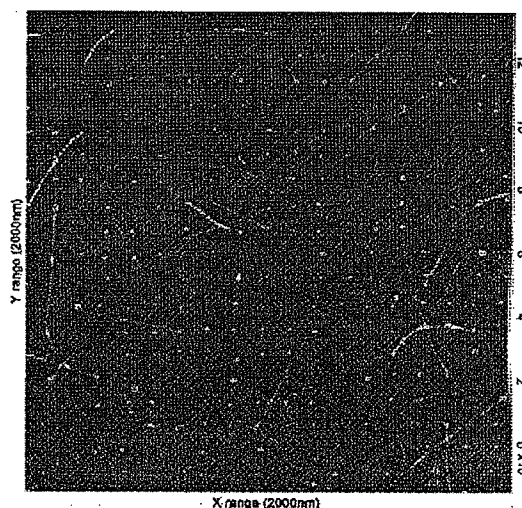

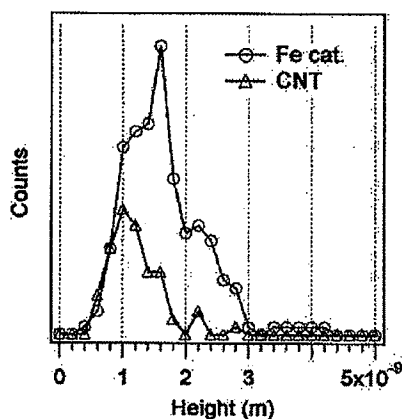Fig. 3. AFM image of CNTs grown from patterned catalyst array (100 nm pitch). Image size is 2 × 2 μm.

Fig. 4. Height distribution of Fe catalyst particles and CNTs grown from Fe catalysts. The average diameter and standard deviation 1σ were 1.7 ± 0.6 nm for Fe catalysts and 1.3 ± 0.4 nm for CNTs, respectively.
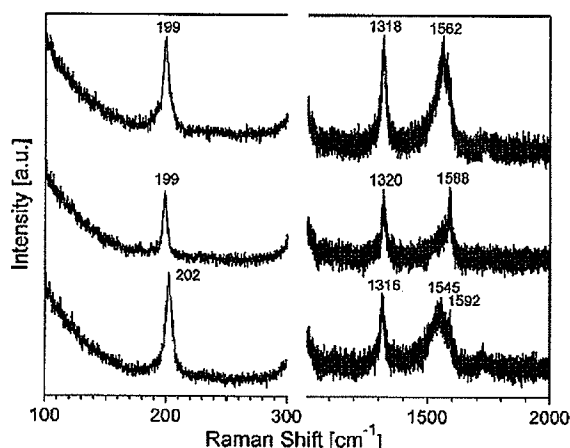

Fig. 5. Raman spectra corrected from three different points using 632.8-nm excitation. Radial breathing mode peaks at $199\,\mathrm{cm}^{-1}$ and $202\,\mathrm{cm}^{-1}$ corresponds to diameters of 1.26 nm and 1.22 nm, respectively.

1-μm laser spot. The RBM peaks only appeared at $199\,\mathrm{cm}^{-1}$ or $202\,\mathrm{cm}^{-1}$, which can be attributed to diameters of 1.26 and 1.22 nm,[17] which corresponds completely to the diameter distribution of CNTs in Fig. 4. These results confirmed the presence of carbon nanotubes. In addition, this diameter range is less than the outer tube diameter of double-walled carbon nanotubes (1.6–2.0 nm).[18] Therefore, they were probably single-walled. The sharp disorder-induced Raman band (D-band) at around $1318\,\mathrm{cm}^{-1}$ was only observed in the spectrum with the RBM peak. This peak might be explained by various symmetry-lowering effects due to end caps, defects, bending, or the finite size of CNTs.[19,20]

In summary, we successfully fabricated an iron nano-particle array with the LANS method. This method yielded an extremely high accuracy in positioning and in size uniformity comparable to the conventional methods. We also carried out CVD growth of CNTs by using the particles as a catalyst. The sharp RBM peak from the sample indicated the presence of SWNTs. We expect that the LANS method opens new possibilities for the nanoparticle research and also provides a practical approach for the integration of devices from CNT building blocks.

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